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Structure and thermal properties of porous polylactic acid membranes prepared via phase inversion induced by hot water droplets

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ABSTRACT

In this study, water droplets generated using an ultrasonic atomizer at room temperature were replaced with water droplets heated to a high temperature (further denoted as hot water droplets) by an electrical heating steam generator during the preparation of porous membranes via phase inversion to reduce the amount of consumed water and fabrication time. As a result, porous polylactic acid (PLA) membranes were successfully prepared, and their microstructure and physical properties were studied by scanning electron microscopy (SEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Further, the effect of the PLA concentration on the morphology and thermal properties of the produced membranes was investigated. The application of hot water droplets significantly improved the exchange rate between the solvent and non-solvent phases, which increased the average pore diameter. Increasing the PLA concentration decreased the pore diameter, and the produced pores became irregular due to the decrease in the mobility of PLA molecules. At the same time, the higher PLA concentrations also increased the thermal stability and crystallinity of the porous membranes which were fabricated without using any toxic coagulants has and thus could be potentially used in tissue engineering and artificial organ development.

1. Introduction

Biodegradable porous membranes prepared from biodegradable polymers have many useful applications in various fields including tissue engineering and artificial organs [1–4]. Usually, they are manufactured by electro-spinning [5], freeze-drying [6], solvent merging/particulate leaching [7,8], and phase inversion techniques [9,10]. Phase inversion is known as one of the most popular membrane fabrication methods due to its ability to produce a porous structure, in which a polymer skeleton is connected to hierarchically arranged pores from the microscale to nanoscale [11,12]. It is usually induced by heating (thermally induced phase separation), water vapor, or non-solvents [13–16]. For example, water induced phase separation was used to fabricate porous polyurethane vascular grafts and porous polyurethane membranes [17–19].

Phase inversion induced by non-solvents is an easy method for producing porous membranes, which involves immersing a polymer solution into a non-solvent bath, leading to the precipitation of polymer species from solution [20,21]. As a result, a bilayer structure containing a dense layer and a porous layer is formed due to the fast exchange between the solvent and non-solvent phases. The dense layer formed during the phase inversion process prevents the migration of liquid or air from one side to another [22]. However, the rapid exchange between the two phases also promotes the formation of finger-like pores, which deteriorate the mechanical properties of the membrane [23]. In order to control the exchange rate between the solvent and non-solvent and thus improve the mechanical properties of the polyurethane porous membrane, an ultrasonic technology was utilized to transform the non-solvent species into micro-droplets, which were subsequently used as

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coagulants for the solidification of the polymer solution. The results of experimental studies revealed that the phase inversion induced by micro-droplets is an ideal preparation method for high-performance porous membranes without dense layers [22,24].

In other works, water micro-droplets generated by an ultrasonic atomizer were used as coagulants to fabricate polylactic acid (PLA) porous membranes, which had many applications in different areas (including wound dressing, drug delivery, bone surgery, medical devices, tissue engineering, surgical sutures, and packaging) due to their excellent biodegradability and biocompatibility [25–27]. The formation of unique S-type clusters was observed on the surface of the PLA porous membranes prepared using water micro-droplets, which were found to be applicable for tissue engineering and artificial organ fabrication after their comparison with the sample prepared using distilled water [28].

However, the preparation of porous membranes via the phase inversion induced by water micro-droplets usually takes a long time because of the low exchange rate between the solvent and the droplets. In order to reduce the preparation time of PLA membranes, water droplets heated to a high temperature (further denoted as hot water droplets) using an electric heating steam generator were used to induce the phase inversion process, and their effect on the membrane morphology was investigated by scanning electron microscopy (SEM). In addition, PLA solutions with different concentrations were used to examine possible morphology changes and the thermal stability of the membranes.

2. Experimental

2.1. Materials and equipment

PLA was purchased from Nature Works LLC., USA. 1,4-dioxane was acquired from Sigma-Aldrich. Double distilled water was produced using a Millipore Milli-Q purification system. A fully automatic electric heating steam generator (NBS-AH) was purchased from Wuhan Nobeth Machinery Manufacturing Co. Ltd.

2.2. Preparation of PLA membranes

Homogeneous PLA solutions with concentrations of 10%, 15%, 20%, and 25% (w/w) were prepared by dissolving an appropriate amount of PLA pellets in 1,4-dioxane during stirring at a temperature of 40 °C followed by degassing under vacuum (with a base pressure of −0.1 MPa) at 25 °C to remove air bubbles. The degassed solutions were cast onto the glass plates (with lengths of 100 mm, widths of 100 mm, and depths of 1 mm) and then placed inside a coagulating container filled with the hot water droplets produced by the electric heating steam generator. The metal tube that connected the coagulating container with the electric heating steam generator was used to supply hot water droplets continuously during the preparation of porous PLA membranes. The suspended droplets dropped onto the surface of PLA solution due to gravity, which induced phase inversion. The solution was kept inside the container filled with hot water droplets for 2 h to form a porous membrane due to coagulation, after which the glass plate with the membrane was taken out and placed in distilled water for 4 h to remove any traces of residual 1,4-dioxane solvent. Subsequently, the membrane was oven-dried at a temperature of 30 ± 2 °C for 72 h to remove residual water. The PLA membrane prepared from 15% PLA solution using water droplets generated by an ultrasonic atomizer at room temperature in accordance with the procedure described in Ref. [28] was utilized as a control sample. Fig. 1 shows the schematic diagram illustrating the preparation of porous PLA membranes via the phase inversion induced by hot water droplets.

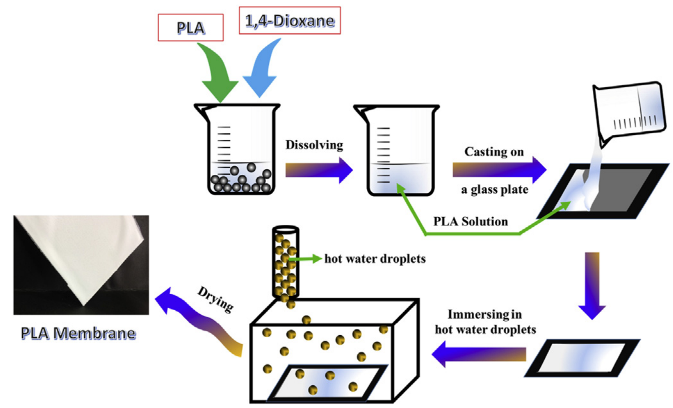

Fig. 1. Schematic diagram illustrating the formation of a porous PLA membrane using hot water droplets.

2.3. Characterization

The prepared membranes were preconditioned inside a conditioning room at a temperature of 25 ± 5 °C and relative humidity of 65 ± 5% for 24 h before characterization by various techniques.

2.4. Porosity measurements

A YG(B)141D fabric thickness gauge (manufactured by Wenzhou Darong Textile Instrument Co., Ltd) with a pressure limit of 50 cN was utilized to determine the thicknesses (D) of the prepared porous PLA membranes by conducting a series of independent measurements (their areas (A) and masses (W_m) were measured separately). The overall porosities of the porous PLA membranes were calculated according to the following reference [22,29].

$$\text{Porosity}(\%) = \frac{V_m - V_p}{V_m} \times 100\% = \left(1 - \frac{W_m}{D \times A \times \rho_P}\right) \times 100\%$$

where V_m is the sample volume; V_p is the polymer volume inside the membrane, which is equal to W_m/ρ_P; and ρ_P is the PLA density of 1.24 g/cm^3. The porosity of each membrane was calculated as the average of the results obtained for three different samples prepared at the same conditions.

2.5. Scanning electron microscopy (SEM)

The surfaces and cross-sectional morphologies of the prepared PLA porous membranes were studied by SEM (JEOL JSM 840A, Tokyo, Japan) at an acceleration voltage of 20 kV and different magnifications. Prior to observations, the SEM samples were fractured under cryogenic conditions using liquid nitrogen, and their surfaces were sputtered with gold. The Image-Pro Plus 6.0 software was used to determine the average pore sizes from the diameters obtained for 50 different pores.

2.6. Thermogravimetric analyzer

The thermogravimetric analysis(TGA) of the prepared PLA porous membranes was performed using an TG 209 F1 instrument (manufactured by Netzsch Group, Germany) in the temperature range from 20 °C to 600 °C at a nitrogen flow rate of 100 mL/min and heating rate of 10 °C/min.